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Olle Heinonen
University of Central Florida

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Stress-induced switching of nonlinear optical properties of linear polymers

Olle Heinonen

Department of Physics, University of Central Florida, Orlando, Florida 32816

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Replacement of every other hydrogen atom in *trans*-polyacetylene by other atoms, such as fluorine, results in a simple linear polymer with two carbon atoms per unit cell of the polymer chain. In such polymers, dimerization can be induced or destroyed reversibly by the application of a uniaxial stress. As a consequence, the nonlinear optical properties can be switched dramatically between those of dimerized chains, which have degenerate ground states, and nondimerized chains, which have a nondegenerate ground state.

Experimental investigations of polymers have shown that some of these materials possess both unusual and large nonlinear optical (NLO) properties.¹ Much attention has been focused on conjugated polymers, and in particular polyacetylene (PA), being the simplest of conjugated polymers. PA has two stable conformations, *trans*-PA and *cis*-PA. Measurements of third-harmonic generation (THG) in PA show that there is a remarkable difference between the THG coefficients of *trans*-PA and *cis*-PA.² Resonant pumping across the optical band gap of *trans*-PA leads to a large shift in the oscillator strength of the optical absorption. This effect is absent in *cis*-PA. Moreover, the nonresonant THG coefficient is 2 orders of magnitude larger in *trans*-PA than in *cis*-PA.

These differences have been explained³ in terms of the Su-Schrieffer-Heeger⁴ model of PA. In this model, *trans*-PA is unstable with respect to a Peierls distortion, which dimerizes the molecule. This leads to a twofold-degenerate ground state (see Fig. 1). The most profound consequence of this degeneracy is that the low-lying excitations are domain walls, or solitons, which are topological defects in the polymer backbone. Associated with each defect is an electronic state with energy in the middle of the band gap. This state can accommodate 0, 1, or 2 electrons. The zero- and two-electron solitons have charges $+e$ and $-e$ respectively, and zero spin. The one-electron soliton, on the other hand, has no charge but spin $\frac{1}{2}$.

In the case of resonant pumping,² photoabsorption creates electron-hole pairs which decay nonradiatively to charged solitons on a time scale of 10^{-13} s. This has as a

consequence that the absorption shifts from the interband energy $\hbar\omega_i$ to the soliton binding energy $\hbar\omega_s$ from the bottom of the conduction band. In the case of nonresonant pumping,² the main contribution to the THG comes from quantum fluctuations³ of the lattice, or virtual soliton-antisoliton pairs. In both resonant and nonresonant pumping, the physical processes responsible for the observed properties are then consequences of the degenerate ground state. Thus, these processes are absent in *cis*-PA, which does not have a degenerate ground state.

The usefulness of PA in actual applications is, however, limited because PA is unstable in air. There has been some effort devoted to synthesizing stable polymers with properties similar to those of PA. One such polymer is poly(monofluoroacetylene) (PMFA), which has recently been synthesized by Botros and Lando.⁵ Some time ago, we presented⁶ a preliminary investigation of the band structure of PMFA. We found that PMFA may or may not dimerize spontaneously, due to a delicate balance between the lattice spring constant κ , the electron-phonon coupling constant α , and the electron hopping integral t_0 . The purpose of the present communications is to demonstrate that the application of a uniaxial stress to PMFA will induce or destroy dimerization reversibly. We estimate the magnitude of the necessary stress to be well within physically accessible ranges. The possibility of reversibly inducing and destroying dimerization has, as a result, that PMFA will exhibit novel NLO properties. In addition, these properties may serve an independent test of the soliton theory of PA.

In Ref. 6 we analyzed PMFA within the tight-binding model. Let $\psi_n(z)$ and $\phi_n(z)$ denote the π orbitals of the carbon-fluorine and carbon-hydrogen units of the n th unit cell along the chain axis, which we take to be the z direction, with orbital energies ϵ_ψ and ϵ_ϕ , respectively (see Fig. 2). The electron hopping integral between these orbitals is t , and the displacements of the carbon atom of the carbon-fluorine unit and that of the carbon atom of the carbon-hydrogen unit in the n th unit cell are denoted v_n and u_n , respectively. In the Born-Oppenheimer approximation these displacements are assumed time independent, and we expand the hopping integral in these

FIG. 1. One of the two degenerate ground states of PA. The other ground state is obtained by interchanging the double and single bonds.

FIG. 2. Schematic figure of PMFA. Carbon atoms reside at each vertex of the zig-zag chain, with alternating fluorine and hydrogen atoms bonded to the carbon atoms. The displacements v_n and u_n of the carbon atoms are along the chain axis in the n th unit cell. The unit cell is boxed by dashed lines.

to first order, giving $t \approx t_0 - \alpha(v_n - u_n)$. For static distortions with the periodicity of the lattice we set $v_n = -v_0$ and $u_n = u_0$. The electron energies E_k are then found to be

$$E_k = -\frac{1}{2}(\epsilon_\phi + \epsilon_\psi) \pm \frac{1}{2}\{(\epsilon_\phi - \epsilon_\psi)^2 + 16[t_0^2 \cos^2(k\alpha) + \alpha^2(v_0 + u_0)^2 \sin^2(k\alpha)]\}^{1/2}, \quad (1)$$

and the band gap E_g

$$E_g = [(\epsilon_\phi - \epsilon_\psi)^2 + 16\alpha^2(u_0 + v_0)^2]^{1/2} \quad (2)$$

and the bandwidth W from the top of the conduction band to the bottom of the valence band is

$$W = [(\epsilon_\phi - \epsilon_\psi)^2 + 16t_0^2]^{1/2}. \quad (3)$$

The energy difference $\epsilon_\phi - \epsilon_\psi$ was calculated to be 0.6 eV and t_0 was found to be 1–2 eV, which is slightly smaller than the value of 3 eV for PA. We argued that the values of κ and α are only slightly smaller than the corresponding values of 21–40 eV/Å² and 4 eV/Å, respectively, for PA.

By minimizing the total energy, the condition for dimerization was found to be

$$\frac{\alpha^2}{\kappa|\epsilon_\phi - \epsilon_\psi|} > \frac{[1 + 16t_0^2/(\epsilon_\phi - \epsilon_\psi)^2]^{1/2}}{2.14 + 2.55 \ln[1 + 16t_0^2/(\epsilon_\phi - \epsilon_\psi)^2]}. \quad (4)$$

With the values $t_0 = 2$ eV, $(\epsilon_\phi - \epsilon_\psi) = 0.6$ eV, and $\alpha = 4$ eV/Å, we found that PMFA dimerizes for $\kappa < 30$ eV/Å². The value of κ is right in the range of the estimated value for κ . We can thus conclude that a small change in κ will induce or destroy dimerization. This will have a profound effect on the NLO properties of PMFA. If it dimerizes, the ground state is degenerate and PMFA is topologically equivalent to *trans*-PA. Its low-lying excitations are then solitons, and the THG of PMFA is in this case similar to that of *trans*-PA, with the difference that the band gap and soliton energies are smaller in PMFA than in PA. Thus, the energies $\hbar\omega_l$ and $\hbar\omega_s$ are red-shifted compared to PA. If PMFA does not dimerize, it still has an energy gap at the Fermi energy due to Bragg scattering at the Brillouin-zone boundaries, but its ground state is nondegenerate. Thus, in this case we expect the NLO properties of PMFA to be similar to those

of a conventional one-dimensional semiconductor.⁷ In particular, as a consequence of the absence of degeneracy of the ground state, there are no soliton excitations, and so no fast shift in the absorption at resonant pumping would be expected. The nonresonant THG will also be smaller in this case, since virtual excitations have to include processes across the band gap, rather than the soliton states.

One possible way to induce and destroy dimerization is by the application of a uniaxial stress along the chain axis. Such a stress will shift the equilibrium separation a along the chain axis between the carbon atoms to $a + \delta a$ with $\delta a/a \ll 1$. As a consequence, κ , α and t_0 will all shift to $\kappa + \delta a(\partial\kappa/\partial a)$, $\alpha + \delta a(\partial\alpha/\partial a)$, and $t_0 + \delta a(\partial t_0/\partial a)$, respectively, where the partial derivatives are evaluated at a separation of a . However, in the condition for dimerization, Eq. (4), only κ enters linearly, and so under the application of a uniaxial stress, this equation becomes approximately

$$\frac{\alpha^2}{\left[\kappa + \delta a \frac{\partial\kappa}{\partial a}\right] |\epsilon_\phi - \epsilon_\psi|} > \frac{[1 + 16t_0^2/(\epsilon_\phi - \epsilon_\psi)^2]^{1/2}}{2.14 + 2.55 \ln[1 + 16t_0^2/(\epsilon_\phi - \epsilon_\psi)^2]}. \quad (5)$$

A change of κ of about 5 eV/Å² may be enough to change the ground state of PMFA. We can estimate the applied stress necessary to shift κ by this amount. We model a chain of PMFA as a diatomic linear array where one kind of atom corresponds to a carbon-fluorine unit, and the other kind corresponds to a carbon-hydrogen unit. The atoms in this array interact with each other through a Lennard-Jones potential,

$$V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}. \quad (6)$$

By only including nearest-neighbor interactions, we can fix the constants A and B by requiring that the equilibrium separation a of the atoms⁶ is that of the carbon atoms in PMFA, $a = 1.22$ Å, and that the spring constant $\kappa = (\partial^2 V/\partial r^2)$ at equilibrium is 30 eV/Å². The partial $\partial\kappa/\partial a$ is then obtained as $\partial^3 V/\partial r^3|_{r=a}$. Using this procedure, we find $\partial\kappa/\partial a \approx -500$ eV/Å³. With the Youngs modulus⁸ of 200 GPa, we then obtain a stress of 2 GPa necessary to induce a shift of κ of 5 eV/Å². This value is well within the range of experimentally accessible values.

In conclusion, we have shown by applying a uniaxial stress of PMFA the ground state may be switched between degenerate (when the polymer is dimerized) and nondegenerate (when the polymer is not dimerized). This has as a consequence that the THG properties of PMFA can be switched between those of *trans*-PA, with a large nonresonant THG and absorption at resonant pumping which shifts from $\hbar\omega_l \approx 0.3$ eV to $\hbar\omega_s \approx 0.15$ eV, to properties similar to those of a conventional one-dimensional semiconductor, with no shift at resonant pumping and a lower nonresonant THG.

It may also be possible to synthesize materials where the switching is accessible at lower stresses and with

more dramatic change in the NLO properties. The characteristics of PMFA that enabled the switching is the fact that PMFA has two carbon atoms per unit cell, so that Bragg reflections at the zone boundaries open up a gap at the Fermi energy whether PMFA is dimerized or not. As a consequence, PMFA is not absolutely unstable with respect to a Peierls distortion, but only conditionally unstable, the conditions being the precise values of the parameters κ , α , and t_0 . Similar materials can be synthesized by replacing the fluorines and the hydrogen by

other atoms.

Finally, the THG of PMFA may serve as an independent verification of the soliton model of PA. The observation of the switching behavior of the THG of PMFA as a function of applied stress would be strong evidence for support of the soliton model.

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¹For example, see D. R. Ulrich, in *Nonlinear Optical and Electroactive Polymers*, edited by P. N. Prasad and D. R. Ulrich (Plenum, New York, 1987).

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